



RECEIVED  
AUG 07 2003  
TC 1700

PATENT 1422-0480P

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

#10  
Mitt  
8-13-03

In Re Application of :  
Shuji TAKANA et al. : Group Art Unit: 1751  
Serial No.: 09/868,141 :  
Filed: June 15, 2001 : Examiner: DOUYON,  
Lorna M.

For: PARTICLES FOR DETERGENT ADDITION

DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF  
PATENTS & TRADEMARKS  
WASHINGTON, D.C. 20231

Sir:

I, Shuji TAKANA, residing in Wakayama-shi, Wakayama-ken, Japan,  
hereby declares and states as follows:

1. That I am one of the co-inventors of U.S. Application Serial No. 09/868,141 filed on June 15, 2001, entitled PARTICLES FOR DETERGENT ADDITION. I am thoroughly familiar with the contents of said Application, its prosecution before the United States Patent and Trademark Office and the references cited therein.
2. That I am a graduate of Kinki University, Faculty of Agriculture in the year 1988, majoring in agrochemistry.
3. That I have been employed in Kao Corporation in the year 1988 and have been assigned to the Research Laboratories.

4. That I have been involved in the research and development of detergent since 1991.

5. That the following experiments were conducted by myself or under my direct supervision and control in order to verify that co-presence of two or more kinds of the water-soluble substances exhibits an unexpectedly superior effects when used in a molar ratio of 9/1 or less.

## METHODS

### Preparation of Comparative Detergent Additive Particles

Comparative Detergent Additive Particles  $\alpha$  were prepared by the process described below.

Four-hundred and fifteen kilograms of water was added to a 1 m<sup>3</sup>-mixing vessel having agitation impellers, and the water temperature was adjusted to 50°C. Two-hundred and fifty kilograms of sodium carbonate and 100 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. Further, the resulting mixture was agitated for 15 minutes with temperature-controlled to 50°C, and thereafter 185 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C, to give a homogeneous slurry.

This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of 25 kg/cm<sup>2</sup>. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 220°C and exhausted from the top of the tower at 108°C. Subsequently, coarse

detergent additive particles obtained from the lower part of the tower were dried with a hot air at 100°C in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 1410 µm-sieve, to give Comparative Detergent Additive Particles α. The composition and the properties of the resulting Comparative Detergent Additive Particles α are shown in Table A.

Incidentally, the microporous capacity at 0.01 to 4 µm was 0.39 mL/g, as determined by a mercury porosimeter for Comparative Detergent Additive Particles α. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 89% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 89% of the particles was 6.0/10.) In addition, Comparative Detergent Additive Particles α were analyzed for a cave-in hole. As a result, the particles were composed of 88% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more, of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 88% of cave-in particles was 26%. In addition, the average depth of the cave-in hole was 57% of the projected area diameter of the particle. In addition, as a result of analyses of Comparative Detergent Additive

Particles  $\alpha$  by FT-IR/PAS and EDS, it was confirmed that the particles had a localized structure in which a higher proportion of zeolite was present in the inner portion of the particle, and higher proportions of the polymer and the water-soluble inorganic salt, which are the water-soluble substances, were present near the particle surface.

Comparative Detergent Additive Particles  $\beta$  were prepared by the process described below.

Four-hundred and fifteen kilograms of water was added to a 1 m<sup>3</sup>-mixing vessel having agitation impellers, and the water temperature was adjusted to 50°C. Two-hundred and fifty kilograms of sodium sulfate and 100 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. Further, the resulting mixture was agitated for 15 minutes with temperature-controlled to 50°C, and thereafter 185 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C, to give a homogeneous slurry.

This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of 25 kg/cm<sup>2</sup>. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 220°C and exhausted from the top of the tower at 109°C. Subsequently, coarse detergent additive particles obtained from the lower part of the tower were dried with a hot air at 100°C in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a

1410  $\mu\text{m}$ -sieve, to give Comparative Detergent Additive Particles  $\beta$ . The composition and the properties of the resulting Comparative Detergent Additive Particles  $\beta$  are shown in Table A.

Incidentally, the microporous capacity at 0.01 to 4  $\mu\text{m}$  was 0.39 mL/g, as determined by a mercury porosimeter for Comparative Detergent Additive Particles  $\beta$ . In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 90% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 90% of the particles was 6.1/10.) In addition, Comparative Detergent Additive Particles  $\beta$  were analyzed for a cave-in hole. As a result, the particles were composed of 86% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more, of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 86% of cave-in particles was 29%. In addition, the average depth of the cave-in hole was 55% of the projected area diameter of the particle. In addition, as a result of analyses of Comparative Detergent Additive Particles  $\beta$  by FT-IR/PAS and EDS, it was confirmed that the particles had a localized structure in which a higher proportion of zeolite was present in the inner portion of the particle, and higher proportions of the polymer and the

water-soluble inorganic salt, which are the water-soluble substances, were present near the particle surface.

Comparative Detergent Additive Particles  $\gamma$  were prepared by the process described below.

Four-hundred and fifteen kilograms of water was added to a  $1\text{ m}^3$ -mixing vessel having agitation impellers, and the water temperature was adjusted to  $50^\circ\text{C}$ . Two-hundred and twenty-five kilograms of sodium carbonate, 25 kg of sodium sulfate, and 100 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. Further, the resulting mixture was agitated for 15 minutes with temperature-controlled to  $50^\circ\text{C}$ , and thereafter 185 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to  $50^\circ\text{C}$ , to give a homogeneous slurry.

This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of  $25\text{ kg/cm}^2$ . A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of  $220^\circ\text{C}$  and exhausted from the top of the tower at  $108^\circ\text{C}$ . Subsequently, coarse detergent additive particles obtained from the lower part of the tower were dried with a hot air at  $100^\circ\text{C}$  in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a  $1410\text{ }\mu\text{m}$ -sieve, to give Comparative Detergent Additive Particles  $\gamma$ . The composition and the properties of the resulting Comparative Detergent Additive Particles  $\gamma$  are shown in Table A.

Incidentally, the microporous capacity at 0.01 to 4  $\mu\text{m}$  was 0.40 mL/g, as determined by a mercury porosimeter for Comparative Detergent Additive Particles  $\gamma$ . In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 93% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 93% of the particles was 5.8/10.) In addition, Comparative Detergent Additive Particles  $\gamma$  were analyzed for a cave-in hole. As a result, the particles were composed of 91% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more, of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 91% of cave-in particles was 24%. In addition, the average depth of the cave-in hole was 61% of the projected area diameter of the particle. In addition, as a result of analyses of Comparative Detergent Additive Particles  $\gamma$  by FT-IR/PAS and EDS, it was confirmed that the particles had a localized structure in which a higher proportion of zeolite was present in the inner portion of the particle, and higher proportions of the polymer and the water-soluble inorganic salt, which are the water-soluble substances, were present near the particle surface.

Preparation of Detergent Particles (b)

Detergent Particles 1 were prepared by the process described below.

A slurry having a water content of 48%, comprising components of each ingredient for Detergent Particles 1 listed in Table B except for 50% by weight of the formulated amount of polyoxyethylene alkyl ether, the entire formulated amount of a crystalline silicate, and 50% by weight of the formulated amount of zeolite, was spray-dried to give spray-dried base material having a bulk density of 310 g/L. Next, the spray-dried base material was supplied into High-Speed Mixer (manufactured by Fukae Powtec Corp., agitation tumbling granulator, equipped with a jacket), and 20% by weight of the formulated amount of the zeolite, and the entire amount of the crystalline silicate were added thereto. The remaining 50% by weight of the formulated amount of the polyoxyethylene alkyl ether heated to 70°C was added by spraying, and the mixture was granulated. Further, the resulting granular product was surface-treated by adding 20% by weight of the formulated amount of the zeolite 60 seconds before the termination of the granulation, to give a granule. Further, the granule was classified with a sieve having a sieve-opening of 1410  $\mu\text{m}$ , and the remaining 10% by weight of the zeolite was added to coarse grains having a size of 1410  $\mu\text{m}$  or more. The resulting mixture was pulverized by Fitz Mill (pulverizer, manufactured by Hosokawa Micron Corporation) to a size of 1410  $\mu\text{m}$  or less, and thereafter the pulverized product was mixed with the sieve-passed granule, to give Detergent Particles 1.

Detergent Particles 2 were prepared by the process described below.



A slurry having a water content of 48%, comprising components of each ingredient for Detergent Particles 2 listed in Table B except for 50% by weight of the formulated amount of polyoxyethylene alkyl ether, the entire formulated amount of a crystalline silicate, and 50% by weight of the formulated amount of zeolite, was spray-dried to give spray-dried base material having a bulk density of 302 g/L. Next, the spray-dried base material was supplied into High-Speed Mixer (manufactured by Fukae Powtec Corp., agitation tumbling granulator, equipped with a jacket), and 20% by weight of the formulated amount of the zeolite, and the entire amount of the crystalline silicate were added thereto. The remaining 50% by weight of the formulated amount of the polyoxyethylene alkyl ether heated to 70°C was added by spraying, and the mixture was granulated. Further, the resulting granular product was surface-treated by adding 20% by weight of the formulated amount of the zeolite 60 seconds before the termination of the granulation, to give a granule. Further, the granule was subjected to the same treatment as in Detergent Particles 1, to give Detergent Particles 2.

Detergent Particles 3 were prepared by the method described below.

A slurry having a water content of 50%, comprising the entire formulated amount of each of sodium polyacrylate, PEG, sodium sulfate, sodium sulfite, a soap and a fluorescent dye, 50% by weight of the formulated amount of zeolite, and 50% by weight of the formulated amount of sodium carbonate, was spray-dried to give spray-dried base material having a bulk density of 460 g/L. The resulting spray-dried base material, the entire formulated amounts of an amorphous aluminosilicate and a crystalline silicate, and the remaining 50% by

weight of the formulated amount of sodium carbonate were supplied into Lödige Mixer, and the agitation was initiated. Heated water at 40°C was allowed to flow through the jacket. The entire formulated amount of the polyoxyethylene alkyl ether heated to 70°C was added by spraying, and the mixture was granulated. Further, the resulting granular product was surface-treated by adding 30% by weight of the formulated amount of the zeolite at the time 60 seconds before the termination of the granulation, to give a granule. The resulting granule was classified with a sieve having a sieve-opening of 1410  $\mu\text{m}$ , and 20% by weight of the formulated amount of the zeolite was added to coarse grains having a size of 1410  $\mu\text{m}$  or more. The resulting mixture was pulverized by a pulverizer (pulverizer, manufactured by Hosokawa Micron Corporation), and thereafter the pulverized product was mixed with the sieve-passed product, to give Detergent Particles 3.

#### Preparation of Composite Detergent Particles

Each group of Comparative Detergent Additive Particles  $\alpha$ ,  $\beta$  and  $\gamma$  was dry-blended with each group of Detergent Particles 1 to 3 for 5 minutes in a V-blender in a weight ratio of 5/95, 10/90 or 30/70, thereby giving composite detergent particles of comparative examples.

Further, based on 99 parts by weight of each group of the above composite detergent particles, 1 part by weight of enzyme granules [0.4 parts by weight of a cellulase ("KAC500," manufactured by Kao Corporation), 0.3 parts by weight of a protease ("Savinase 12.0T-W," manufactured by NOVO Nordisk), and 0.3 parts by weight of a lipase ("Lipolase 100T," manufactured by NOVO

Nordisk)] were additionally added, and the resulting mixture was dry-blended for 5 minutes in the V-blender, to give a granular detergent composition of a comparative example.

The granular detergent compositions obtained as above were evaluated for the distributivity in a dispenser of a drum-type washing machine by the following method.

[Evaluation of Distributivity in Dispenser]

Twenty grams of a granular detergent composition was placed in a dried detergent-supplying case of a drum-type washing machine "ES-E60," manufactured by Sharp Corporation, and tap water at 20°C was poured into an empty drum. After pouring water was ended, the granular detergent composition remaining in the detergent-supplying case was recovered. The weight of the composition after drying at 105°C for 4 hours was measured, and the remaining ratio was calculated by the following equation.

$$\text{Remaining Ratio (\%)} = 100 \times \frac{(\text{Dry Weight of Residue (g)})}{20 \text{ (g)}}$$

The results of the evaluation (remaining ratios) of each of the granular detergent compositions in which Comparative Detergent Additive Particles  $\alpha$ ,  $\beta$  and  $\gamma$  were used are shown in Table C.

Also, the evaluation results of distributivity in dispenser for Examples of the present invention using Detergent Additive Particles 1 to 5 in which sodium sulfate and sodium carbonate were mixed at a molar ratio of 9/1 or less, which

are summarized from Table 3 of the present specification, are shown in Table D. It is clear from the results shown in Tables C and D that each of the granular detergent composition, in which Detergent Additive Particles 1 to 5 were used, has markedly excellent distributivity as compared with those of Comparative Examples in which Comparative Detergent Additive Particles  $\alpha$ ,  $\beta$  and  $\gamma$  were used.

Specifically, it is evident that from Table C that not only in a case of Comparative Detergent Additive Particle  $\alpha$  or  $\beta$  where either sodium carbonate or sodium sulfate is used, but also in a case of Comparative Detergent Additive Particles  $\gamma$  where both sodium carbonate and sodium sulfate are used in a molar ratio outside the range of 9/1 or less, the effects are drastically worsened as compared to the effects of the present invention shown in Table D. Incidentally, the molar ratio of sodium carbonate to sodium sulfate is about 12/1 in Comparative Detergent Additive Particles  $\gamma$ , of which ratio corresponds to Example 1 of Appel (U.S. Patent 6,069,124) where a molar ratio of sodium sesquicarbonate to other water-soluble substances is about 12/1. In other words, the effects of the present invention would not be obtained in the invention of Appel.

Table A

	Comparative Detergent Additive Particles		
	$\alpha$	$\beta$	$\gamma$
<u>Formulating Composition</u> (% by weight)			
LAS-Na <sup>1)</sup>			
Polyoxyethylene Alkyl Ether <sup>2)</sup>			
Sodium Carbonate <sup>3)</sup>	50		45
Sodium Sulfate <sup>4)</sup>		50	5
Sodium Polyacrylate <sup>5)</sup>	8	8	8
Zeolite <sup>6)</sup>	37	37	37
Water	5	5	5
Sodium Percarbonate Granule			
Enzyme Granule			
<u>Properties</u>			
Bulk Density (g/L)	565	560	563
Average Particle Size ( $\mu\text{m}$ )	273	281	275
Dissolution Rate (%) at 5°C after 60 seconds	96	94	96
Microporous Capacity (mL/g)	0.39	0.39	0.4
Ratio of Bubble Generation (%)	89	90	93
Ratio of Cave-in Particle (%)	88	86	91
Localized Structure	Yes	Yes	Yes

1): NEOPELEX F65 (manufactured by Kao Corporation)

2): EMULGEN 108 KM, average moles of ethylene oxides: 8.5 (manufactured by Kao Corporation)

3): DENSE ASH (manufactured by Central Glass Co., Ltd.)

4): Anhydrous neutral sodium sulfate (manufactured by Shikoku Kasei K.K.)

5): Average molecular weight: 10000

6): Zeolite 4A-type, average particle size: 3.5  $\mu\text{m}$  (manufactured by Tosoh Corporation)

Table B

	Detergent Particles		
	1	2	3
<u>Formulating Composition (% by weight)</u>			
LAS-Na <sup>1)</sup>	23	25.6	
AS-Na <sup>7)</sup>	7	7.8	
Polyoxyethylene Alkyl Ether <sup>2)</sup>	4	4.4	20
Soap <sup>8)</sup>	3	3.3	5
PEG <sup>9)</sup>	2	2.2	2
No. 1 Sodium Silicate <sup>10)</sup>	10	11.1	
Crystalline Silicate <sup>11)</sup>	5	5.6	24
Zeolite <sup>6)</sup>	25	23.7	18
Amorphous Aluminosilicate <sup>12)</sup>			10
Sodium Carbonate <sup>3)</sup>	9	7.4	10
Sodium Sulfate <sup>4)</sup>	3	0.3	3
Sodium Sulfite <sup>13)</sup>	0.5	0.6	0.5
Sodium Polyacrylate <sup>5)</sup>	3	2.4	5
Fluorescent Dye <sup>14)</sup>	0.5	0.6	0.5
Water	5	5	2
<u>Properties</u>			
Bulk Density (g/L)	785	776	820
Average Particle Size (μm)	394	412	355

1) to 6) are the same as in Table 1.

7): Alkylsulfate having 12 to 18 carbon atoms

8): Sodium salt of fatty acid of beef tallow (14 to 18 carbon atoms)

9): Polyethylene glycol (average molecular weight: 10000)

10): No. 1 sodium silicate (manufactured by Tosoh Corp., solid content: 44% by wt.)

11): Product prepared by pulverizing SKS-6 (manufactured by Clariant Tokuyama, average particle size: 120 μm) by a roll mill (average particle size: 8 μm)

12): Product described in Preparation Example 2 of Japanese Patent Laid-Open No. Hei 9-132794 (average particle size: 8 μm)

13): Sodium Sulfite (manufactured by Mitsui Toatsu K.K.)

14): Mixture of Tinopal CBS-X and Tinopal AMS-GX (manufactured by Ciba Specialty Chemicals K.K.) in the weight ratio of 1:1

Table C

(Comparative Detergent Additive Particles)/Detergent  
Particles = 5/95 (weight ratio)

	Comp. Ex. Comparative Additive Particles $\alpha$	Comp. Ex. Comparative Additive Particles $\beta$	Comp. Ex. Comparative Additive Particles $\gamma$
Detergent Particles 1	45%	30%	41%
Detergent Particles 2	34%	35%	30%
Detergent Particles 3	41%	45%	44%

(Comparative Detergent Additive Particles)/Detergent  
Particles = 10/90 (weight ratio)

	Comp. Ex. Comparative Additive Particles $\alpha$	Comp. Ex. Comparative Additive Particles $\beta$	Comp. Ex. Comparative Additive Particles $\gamma$
Detergent Particles 1	49%	53%	51%
Detergent Particles 2	54%	58%	47%
Detergent Particles 3	40%	53%	50%

(Comparative Detergent Additive Particles)/Detergent  
Particles = 30/70 (weight ratio)

	Comp. Ex. Comparative Additive Particles $\alpha$	Comp. Ex. Comparative Additive Particles $\beta$	Comp. Ex. Comparative Additive Particles $\gamma$
Detergent Particles 1	43%	48%	45%
Detergent Particles 2	35%	52%	41%
Detergent Particles 3	46%	43%	38%

Table D

(Detergent Additive Particles)/Detergent Particles = 5/95 (weight ratio)

	Example Additive Particles 1	Example Additive Particles 2	Example Additive Particles 3	Example Additive Particles 4	Example Additive Particles 5
Detergent Particles 1	2%	8%	0%	7%	18%
Detergent Particles 2	3%	6%	0%	5%	14%
Detergent Particles 3	3%	6%	0%	9%	17%

(Detergent Additive Particles)/Detergent Particles = 10/90 (weight ratio)

	Example Additive Particles 1	Example Additive Particles 2	Example Additive Particles 3	Example Additive Particles 4	Example Additive Particles 5
Detergent Particles 1	0%	2%	0%	1%	9%
Detergent Particles 2	0%	1%	0%	0%	10%
Detergent Particles 3	0%	2%	0%	3%	6%

(Detergent Additive Particles)/Detergent Particles = 30/70 (weight ratio)

	Example Additive Particles 1	Example Additive Particles 2	Example Additive Particles 3	Example Additive Particles 4	Example Additive Particles 5
Detergent Particles 1	0%	0%	0%	0%	2%
Detergent Particles 2	0%	0%	0%	0%	0%
Detergent Particles 3	0%	0%	0%	0%	2%



6. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

7. Further declarant saith not.

Shuji Takanaka  
Shuji TAKANA

July 18, 2003  
Date